

Bistable anchoring of nematics on rough substrates

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Abstract. – We analyze the interplay between wetting and anchoring of nematic liquid crystals on disordering, *e.g.*, rough substrates in the framework of the Landau-de Gennes theory, in situations of competing homeotropic and planar easy axes on the substrate and the nematic-isotropic (NI) interface. The phase diagram for azimuthally symmetric substrates is calculated. We identify two regimes - a strongly coupled regime, where the wetting transition coincides with an anchoring transition, and a weakly coupled regime, where the two are separated. The anchoring transition is first order and switches between homeotropic and planar anchoring. The two competing orientations are metastable over a broad parameter range. Hence such surfaces can be used to generate bistable surfaces.

Nematic liquid crystals are fluids of aligned particles with a preferred orientation [1]. In the bulk, the direction of alignment is arbitrary, but surfaces break the isotropy of space and tend to align nematic fluids. This phenomenon, called surface anchoring, is of both fundamental and industrial interest, *e.g.*, in liquid display technology [2, 3]. From the practical point of view, it is useful to have surfaces which favor two orientations, such that one can effortlessly switch from one to another. Various strategies have been proposed to obtain such bistable surfaces [4–10]. Here, we analyze a mechanism that generates bistability on rough substrates.

Experiments [11–13], theory [14], as well as simulations [15, 16] have shown that rough or nanostructured substrates can reduce the order at the surface and even depress the NI transition in confined systems. If the disordering effect of a substrate is strong enough to nucleate a surface layer of strongly reduced order, the adjacent nematic fluid is oriented by that layer rather than by the bare substrate [12], and the direction of alignment may change. For example, Simoni *et al.* have observed experimentally that a porous polymeric substrate imprints a different orientation on a nematic film than a flat substrate made of the same material [17]. In their system, the alignment was homeotropic on the flat substrate, but planar on the porous substrate. This effect can be understood quite naturally if one assumes that the substrate favors homeotropic alignment, and the NI interface induces planar alignment.

The question is whether the effect can be used to generate bistable surfaces. Rodriguez-Ponce *et al.* [18] have carried out density functional calculations for a model liquid crystal on a disordering substrate in a similar situation of competing, planar and homeotropic, anchoring axes. Encouragingly, they find a first order anchoring transition between planar and

homeotropic anchoring. The anchoring transition seems related to wetting, but the exact nature of the relation is not clear: The system also exhibits wetting transitions that are not connected to an anchoring transition, and even reentrant wetting. In the present work, we present an analysis of the problem in the general framework of the Landau-de Gennes theory. We clarify in detail the relation between the anchoring transition and the wetting transition, and identify different regimes of weak and strong coupling, which establish the context for the findings of Rodriguez *et al.* We find that the anchoring transition is first order, and that there exists a broad intermediate regime, where both anchoring orientations are at least metastable and the system can easily switch from one to the other. Hence these surfaces should be suitable candidates for bistable surfaces.

The fact that competing easy axes may influence wetting phenomena has first been pointed out for *nematic* wetting layers by Sullivan and Lipowsky [19]. Director distortions in nematic wetting layer may lead to long-range interactions between the substrate and the NI interface. The consequences for the wetting phase behavior have been analyzed within the Landau-de Gennes theory by Braun *et al.* [20], using a formalism originally developed by Sen and Sullivan [21]. Within the same framework, Teixeira *et al.* [22] have studied a system with an isotropic wetting layer. This work is related to ours, but the system is much more complicated. Already the bare substrate free energy has two competing contributions: A term which is linear in the order parameter and favors surface order and homeotropic anchoring, and a quadratic disordering term which favors *conical* anchoring. As a result, a continuous surface driven anchoring transition from conical to homeotropic was found for a set of parameters with strong linear term, and a first order wetting driven anchoring transition from conical to planar for a second set with weak linear term. Here, we shall focus on the simpler case of a purely disordering substrate that favors homeotropic anchoring.

Our starting point is the Landau-de Gennes theory of nematic liquid crystals, which is based on a free energy expansion in powers of a symmetric and traceless (3×3) order tensor field $\mathbf{Q}(\mathbf{r})$. The leading terms contributing to the bulk free energy are [1]

$$F_{\text{bulk}} = \int d^3r \left\{ \frac{A}{2} \text{Tr}(\mathbf{Q}^2) + \frac{B}{3} \text{Tr}(\mathbf{Q}^3) + \frac{C}{4} \text{Tr}(\mathbf{Q}^2)^2 + \frac{L_1}{2} \partial_i Q_{jk} \partial_i Q_{jk} + \frac{L_2}{2} \partial_i Q_{ij} \partial_k Q_{kj} \right\}. \quad (1)$$

For simplicity, we neglect the biaxiality and approximate the order tensor by [23] $Q_{ij}(\mathbf{r}) = \frac{1}{2} S(\mathbf{r})(3n_i(\mathbf{r})n_j(\mathbf{r}) - \delta_{ij})$, where $S(\mathbf{r})$ is the local nematic order parameter, and $\mathbf{n}(\mathbf{r})$ the director, a vector of length unity describing the local direction of alignment. This is justified by the fact that homeotropically orienting surfaces do not induce biaxiality, and that the biaxiality induced by the NI interface is small [24,25]. Furthermore, we introduce the ‘‘natural’’ units $\hat{S} = -2B/9C$, $\hat{\xi} = 2\sqrt{(L_1 + L_2/6)}/3C \hat{S}^{-1}$, and $\hat{\epsilon} = (3C/16) \cdot \hat{S}^4 \hat{\xi}^3$. The quantity \hat{S} is the value of the order parameter in the nematic phase at coexistence, $\hat{\xi}$ is the minimum width of a planar NI interface at coexistence, and $\hat{\epsilon}/\hat{\xi}^2$ the corresponding interfacial tension. In the following, all order parameters, lengths, and energies, shall be rescaled by these units. This leaves us with two dimensionless parameters,

$$t = \frac{1}{4} A \frac{\hat{S}^2 \hat{\xi}^3}{\hat{\epsilon}} - 1, \quad \text{and} \quad \alpha = \frac{1}{2} \frac{L_2}{(L_1 + L_2/6)}. \quad (2)$$

The parameter t is proportional to the distance to NI coexistence in the phase diagram - *i.e.*, the temperature distance ($t \propto (T - T_{NI})$) in thermotropic liquid crystals, or the chemical potential distance ($t \propto (\mu - \mu_{NI})/T_{NI}$) in lyotropic liquid crystals. The parameter α characterizes the anchoring strength of a planar NI interface. At $\alpha > 0$, the interface favors parallel, planar alignment, and at $\alpha < 0$, it favors perpendicular, homeotropic alignment.

The resulting rescaled bulk free energy takes the form

$$\begin{aligned}
F_{\text{bulk}} &= 3 \int d^3r \{f + g_1 + g_2\} \quad \text{with} \quad f = S^2((S-1)^2 + t), \\
g_1 &= \left((\nabla \cdot S)^2 + \alpha(\mathbf{n} \cdot \nabla S)^2 \right) + 4\alpha S \left((\nabla \cdot \mathbf{n})(\mathbf{n} \cdot \nabla S) + \frac{1}{2}(\mathbf{n} \times \nabla \times \mathbf{n})(\nabla S) \right), \\
g_2 &= S^2 \left((3+2\alpha)(\nabla \mathbf{n})^2 + (3-\alpha)(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + (3+2\alpha)(\mathbf{n} \times \nabla \times \mathbf{n})^2 \right).
\end{aligned} \tag{3}$$

The first term, $f(S)$, describes the free energy density of a homogeneous system, the middle term accounts for the effect of order parameter variations, and the last term corresponds to the Frank elastic energy of a nematic phase with spatially varying director [1]. This term, g_2 , allows to relate the parameter α to the experimentally accessible Frank elastic constants K_i of a material. For example, for MBBA, one has $K_3/K_2 = (3+2\alpha)/(3-\alpha) \approx 3$, *i.e.*, $\alpha \approx 1.2$.

Next, we must determine the appropriate surface free energy. An isotropic surface introduces only one symmetry breaking vector, the surface normal \mathbf{n}_0 . This vector can be combined with \mathbf{Q} to construct the surface energy terms that are compatible with the symmetry of the system [26]. The linear order term in \mathbf{Q} , $\mathbf{n}_0 \mathbf{Q} \mathbf{n}_0 = \frac{3}{2}S(\mathbf{n}\mathbf{n}_0)^2 - \frac{1}{2}S$, favors nematic order, *i.e.*, a surface free energy containing such a term will always be minimized by a nonzero value of S . Hence this term must vanish close to a truly disordering surface. To quadratic order in \mathbf{Q} , one obtains three terms, from which one can construct the general expression

$$F_{\text{surf}} = \int d^2r f_{\text{surf}} \quad \text{with} \quad f_{\text{surf}} = WS^2(1 + \beta n_{\parallel}^2 + \gamma n_{\parallel}^4) \quad \text{and} \quad n_{\parallel}^2 := 1 - (\mathbf{n}\mathbf{n}_0)^2. \tag{4}$$

At $W > 0$ and $\beta > 0$, the surface favors $S = 0$ (disorder) and $n_{\parallel} = 0$ (homeotropic alignment). The parameter $W > 0$ measures the disordering effect of the substrate, *i.e.*, it's roughness, and the parameter $\beta > 0$ characterizes it's orienting strength. For $\gamma < -\beta/2$, the surface has an additional preference for planar anchoring. In the following, we shall assume $\gamma = 0$ for simplicity. It is worth noting that the form (4) of f_{surf} already implies that the wetting transition *must* be second order, for symmetry reasons, unless it is coupled with an anchoring transition [27].

The total free energy is given by $F = F_{\text{bulk}} + F_{\text{surf}}$, with F_{bulk} and F_{surf} given by Eqs. (3) and (4). Our task is to minimize this functional with respect to the profiles $S(\mathbf{r})$ and $\mathbf{n}(\mathbf{r})$. We take the surface to lie in the (xy) plane, hence we can assume that the profiles vary only in the z direction. After parametrizing the director \mathbf{n} as $\mathbf{n} = (n_{\parallel} \cos \phi, n_{\parallel} \sin \phi, n_z)$ with $n_{\parallel}^2 + n_z^2 = 1$, one checks easily that F as a function of n_z and ϕ is minimized by $d\phi/dz \equiv 0$: The director does not vary in the azimuthal direction. Hence we are left with two profiles, $S(z)$ and $n_z(z)$, which have to be determined such that they minimize the total free energy.

We will now sketch a method that allows to solve this and similar problems very efficiently. We divide the order parameter $S(z)$ profile in piecewise monotonic parts. (In our case, the whole profile was monotonically increasing). For each part, we rewrite the director profile as a function of the order parameter S , $n_z(z) \equiv n_z(S)$. After introducing new variables $q = \ln(S)$ and $\psi = 2 \arcsin(n_z)$ for convenience, the bulk free energy (3) per surface area A can be written

$$\begin{aligned}
\frac{F_{\text{bulk}}}{A} &= 3 \int_0^{\infty} dz \left\{ f(e^q) + \left(\frac{dq}{dz} \right)^2 e^{2q} \Phi^2(\psi, \frac{d\psi}{dq}) \right\} \\
\text{with} \quad \Phi^2(\psi, \psi') &= 1 + \frac{\alpha}{2}(1 - \cos \psi) + \frac{\alpha}{2}\psi' \sin \psi + \frac{3+2\alpha}{4}\psi'^2.
\end{aligned} \tag{5}$$

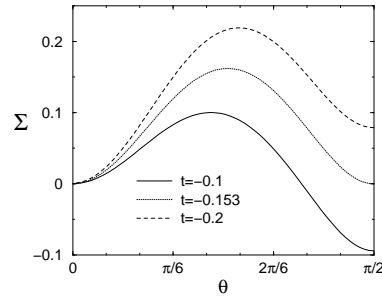


Fig. 1 – Examples of effective anchoring potentials Σ as a function of the anchoring angle θ between the director and the surface normal. The parameters are $W = 2.5$, $\alpha = 1.2$, $\beta = 1.$, and t as indicated.

It is first minimized with respect to $q(z)$ for given $\psi(q)$. The Euler-Lagrange equations yield the integration constant $f(e^q) - (dq/dz)^2 e^{2q} \Phi^2 = \text{const.} = f_\infty$, where $f_\infty = f(S_{\text{nematic}})$ is the free energy density in the homogeneous nematic bulk. This can be used to derive an expression for dq/dz , which can be inserted into the total free energy, yielding

$$F/A = V f_\infty/A + 6 \int_{q_0}^{q_\infty} dq e^q \sqrt{f(e^q) - f_\infty} \Phi(\psi, \psi') + f_{\text{surf}} \quad (6)$$

with $f_{\text{surf}} = W e^{2q_0} (1 + \beta \cos^2(\psi_0/2) + \gamma \cos^4(\psi_0/2))$. The index ∞ stands for the bulk, the index 0 for the surface, and V is the total volume of the system. The free energy (6) can now be minimized with respect to $\psi(q)$. A variational treatment yields the Euler-Lagrange equation

$$\psi'' \frac{\partial^2 \Phi}{\partial \psi'^2} = \frac{\partial \Phi}{\partial \psi} - \frac{\partial^2 \Phi}{\partial \psi \partial \psi'} \psi' - \left(1 + \frac{1}{2} \frac{d}{dq} \ln(f(e^q) - f_\infty)\right) \frac{\partial \Phi}{\partial \psi'}, \quad (7)$$

$$\text{with boundary conditions} \quad \left. \frac{\partial \Phi}{\partial \psi'} \right|_{q_\infty} = 0, \quad q_\infty = \ln(S_{\text{nematic}}), \quad (8)$$

$$\text{and} \quad 6e^{q_0} \sqrt{f(e^{q_0}) - f_\infty} \left. \frac{\partial \Phi}{\partial \psi'} \right|_{q_0} = \left. \frac{\partial f_{\text{surf}}}{\partial \psi} \right|_{q_0}, \quad 6e^{q_0} \sqrt{f(e^{q_0}) - f_\infty} \Phi(\psi_0, \psi'_0) = \left. \frac{\partial f_{\text{surf}}}{\partial q} \right|_{\psi_0} \quad (9)$$

Eq. (8) (left) was obtained by minimizing (6) for arbitrary upper integration limit $q_{\text{max}} < q_\infty$, and then taking the limit $q_{\text{max}} \rightarrow q_\infty$. One easily checks that both $\psi \equiv 0$ and $\psi \equiv \pi$ are solutions of Eqns. (7)-(9). To calculate the anchoring potential for arbitrary anchoring angle θ , we fix $\psi_\infty = \pi - 2\theta$, calculate ψ'_∞ from Eq. (8), and perform a straightforward integration of Eq. (7), starting at q_∞ and stopping as soon as Eq. (9) (right) is fulfilled. The resulting total free energy per area $F/A \equiv \Sigma$ gives the anchoring potential. At the extrema of Σ , the remaining boundary condition (9) (left) is automatically fulfilled.

Some examples of anchoring potentials $\Sigma(\theta)$ are shown in Fig. 1. As a rule, the anchoring potential always assumed it's minimum either at $\theta = 0$ (homeotropic anchoring) or $\theta = \pi/2$ (planar anchoring) [28]. Far from the NI coexistence and for weakly disordering substrates (low W), the orienting force of the substrate dominates and the effective anchoring is homeotropic. Close to the coexistence and for strongly disordering substrates (high W), the main orienting force stems from the fluid layer with strongly varying order parameter close to the surface. In that case, the effective anchoring is planar. Fig. 2 shows two examples of phase diagrams in the (W, t) plane. At the transition lines, the surface is truly bistable, both homeotropic

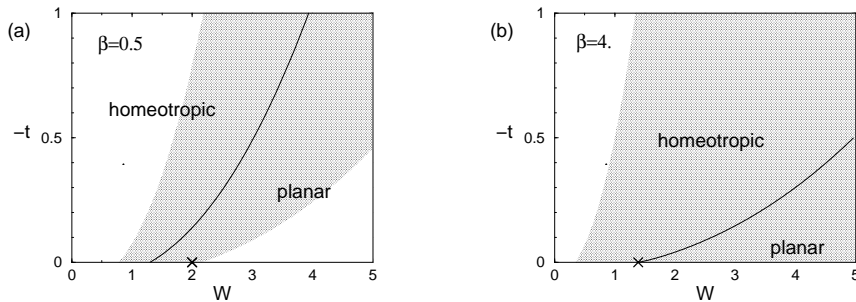


Fig. 2 – Anchoring phase diagrams in the (W, t) plane (distance from NI coexistence $(-t)$ vs. surface roughness W), for two values of the substrate orienting strength β , at $\alpha = 1.2$. The solid lines mark the phase transition, and the hatched areas indicate the parameter regions where both planar and homeotropic anchoring are at least metastable. The cross indicates the position of the wetting transition at $t = 0$. If one increases W at $t = 0$ for small β ($\beta < \beta^* = 1.16$), one first encounters a first order homeotropic/planar transition, and then a second order wetting transition. For large β ($\beta > \beta^*$), the homeotropic/planar transition triggers the wetting transition, which is then first order.

and planar alignment are equally favorable. For practical purposes, it will often be sufficient if a state is metastable, *i.e.*, if it corresponds to a minimum of $F(\theta)$. Fig. 2 shows that the regions where both states are metastable (hatched areas) are quite large. Moreover, the energy barriers between the two states are small ($\sim 0.1\hat{\epsilon}/\hat{\xi}^2$, see Fig. 1), hence switching between the two states is easy.

For a more thorough understanding of this transition, we must relate it to the wetting transition. Thus we consider the two competing states, $\theta = \pi/2$ and $\theta = 0$ at NI coexistence ($t = 0$). The resulting free energy as a function of the surface order parameter, S_0 , is

$$\Sigma = \begin{cases} (1 - S_0)^2(1 + 2S_0) + (1 + \beta) W S_0^2 & \text{planar} \\ \sqrt{1 + \alpha} (1 - S_0)^2(1 + 2S_0) + W S_0^2 & \text{homeotropic.} \end{cases} \quad (10)$$

If Σ takes its minimum at $S_0 = 0$, the surface is wetted by the isotropic phase; otherwise, it is nonwet. For fixed anchoring angle, the wetting transition hence takes place at $W_p^* = 3/(1 + \beta)$ in the planar case, and at $W_h^* = 3\sqrt{1 + \alpha}$ in the homeotropic case, and it is continuous (critical wetting). In addition, the system may switch from the homeotropic state to the planar state. As expected, the wet surface always favors planar anchoring.

The resulting phase behavior depends on the orienting strength β of the surface. If $|\beta|$ is larger than a critical value $|\beta^*|$, the anchoring is homeotropic for all nonwet surfaces. The transition from homeotropic to planar anchoring coincides with the wetting transition, and is first order. For smaller $|\beta|$, the (first order) homeotropic-planar transition preempts the wetting transition, which is then continuous. In this case, the system switches to planar anchoring at a stage where the NI interface is not yet fully developed. Fig. 3 shows the wetting phase diagram for $\alpha = 1.2$ and, more generally, the value β^* which separates the two regimes as a function of α .

Rough, bistable, surfaces can be combined with conventional smooth or rubbed surfaces in a nematic liquid crystal cell device. As an example, we briefly discuss the phase diagrams of a nematic fluid confined between a bistable surface, and strongly orienting surfaces with fixed anchoring angle $\theta_S = 0$ (homeotropic) or $\theta_S = \pi/2$ (planar). Since $S \equiv S_\infty$ in the cell, the only relevant contribution to the bulk free energy, (3), is the Frank elastic energy

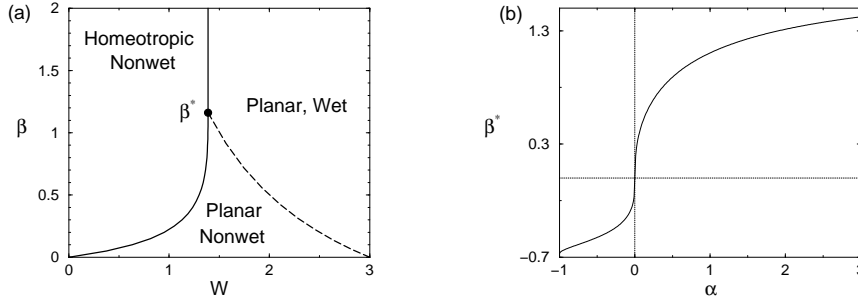


Fig. 3 – (a) Wetting phase diagram at coexistence ($t = 0$) for $\alpha = 1.2$. Solid lines correspond to first order, dashed line to continuous transitions. For $|\beta| < |\beta^*|$, the planar/homeotropic phase transition and the wetting transition are separated; for $|\beta| > |\beta^*|$, they coincide. (b) Critical value β^* where the wetting and the anchoring transitions meet as a function of α . Here, results are also shown for the case $\alpha, \beta < 0$, where the surface favors planar alignment and the NI interface aligns homeotropically.

g_2 , and we can write the total free energy per area of the system as $F_{\text{cell}}/A = \Sigma(\theta_R) + 3(3 + 2\alpha) S_\infty^2 (\theta_S - \theta_R)^2/D$. Here θ_R is the anchoring angle on the rough surface, and D is the thickness of the film. This must be minimized with respect to θ_R . The phase diagrams for a system with the same surface parameters as in Fig. 1 are shown in Fig. 4. The system can assume two different configurations - a homogeneous configuration with fixed director angle, $\theta \equiv \theta_R$ throughout the system, and a hybrid aligned nematic (HAN) configuration where the director slowly rotates from the planar to the homeotropic orientation in the z -direction. The transition lines between the different states can be calculated to a very good approximation, if one assumes that θ_R can only take the values $\theta_R = 0$ or $\theta_R = \pi/2$ (dashed lines in Fig. 4). Hence the rough surface really acts like a two-state surface.

To summarize, we have analyzed the interplay of wetting and anchoring on disordering substrates within the Landau-de Gennes theory in situations of competing, homeotropic and planar, anchoring axes at the substrate and the NI interface. We have identified different

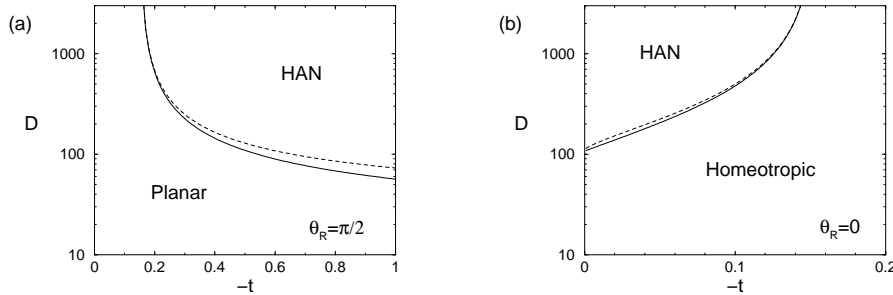


Fig. 4 – Phase diagrams of a nematic liquid crystal confined between a bistable surface and a strongly anchoring surface with anchoring angle $\theta_R = \pi/2$ (a) and $\theta_R = 0$ (b). HAN denotes a “hybrid aligned nematic” state where the director rotates from homeotropic to planar alignment. The two other states correspond to homogeneous planar or homogeneous homeotropic alignment. The thick solid lines indicate the exact transition lines, dashed lines an approximative result as explained in the text. The parameters of the bistable surface are $W = 2.5$, $\alpha = 1.2$, $\beta = 1$.

substrate regimes – one “strongly orienting” regime where the anchoring transition coincides with the wetting transition, and one “weakly orienting” regime where it preempts the wetting transition. The anchoring transition is first order, but the wetting transition must be continuous, if it is not coupled with an anchoring transition. Finally, we have discussed how this effect can be used to design bistable surfaces, which favor two distinctly different orientations, and given an example how such a surface could be integrated in a nematic liquid crystal cell. The present study is a mean field study, the effect of fluctuations has been disregarded. Two types of fluctuations will renormalize the surface potential: Director fluctuations become increasingly important close to the NI transition [29], and fluctuations of the NI interface [30] become important at complete wetting. It will be interesting to study the influence of these effects in future work.

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